



## The adsorption of plutonium IV and V on goethite

ARTHUR L. SANCHEZ<sup>1,3</sup>, JAMES W. MURRAY<sup>1</sup> and THOMAS H. SIBLEY<sup>2</sup>

<sup>1</sup> School of Oceanography, University of Washington, Seattle, WA 98195

<sup>2</sup> School of Fisheries, University of Washington, Seattle, WA 98195

<sup>3</sup> Present address: Graduate School of Public Health, University of Pittsburgh, Pittsburgh, PA 15261

(Received November 28, 1984; accepted in revised form July 23, 1985)

**Abstract**—The adsorption of Pu(IV) and Pu(V) on goethite ( $\alpha\text{FeOOH}$ ) from  $\text{NaNO}_3$  solution shows distinct differences related to the different hydrolytic character of these two oxidation states. Under similar solution conditions, the adsorption edge of the more strongly hydrolyzable Pu(IV) occurs in the pH range 3 to 5 while that for Pu(V) is at pH 5 to 7. The adsorption edge for Pu(V) shifts with time to lower pH values and this appears to be due to the reduction of Pu(V) to Pu(IV) in the presence of the goethite surface. These results suggest that redox transformations may be an important aspect of Pu adsorption chemistry and the resulting scavenging of Pu from natural waters.

Increasing ionic strength (from 0.1 M to 3 M NaCl or  $\text{NaNO}_3$  and 0.03 M to 0.3 M  $\text{Na}_2\text{SO}_4$ ) did not influence Pu(IV) or Pu(V) adsorption. In the presence of dissolved organic carbon (DOC), Pu(V) reduction to Pu(IV) occurred in solution. Pu(IV) adsorption on goethite decreased by 30% in the presence of 240 ppm natural DOC found in Soap Lake, Washington waters. Increasing concentrations of carbonate ligands decreased Pu(IV) and Pu(V) adsorption on goethite, with an alkalinity of 1000 meq/l totally inhibiting adsorption.

The Pu-goethite adsorption system provides the data base for developing a thermodynamic model of Pu interaction with an oxide surface and with dissolved ligands, using the MINEQL computer program. From the model calculations we determined equilibrium constants for the adsorption of Pu(IV) hydrolysis species. The model was then applied to Pu adsorption in carbonate media to see how the presence of  $\text{CO}_3^{2-}$  could influence the mobility of Pu. The decrease in adsorption appears to be due to formation of a Pu- $\text{CO}_3$  complex. Model calculations were used to predict what the adsorption curves would look like if Pu- $\text{CO}_3$  complexes formed.

### INTRODUCTION

ADSORPTION ONTO suspended particulate matter has been suggested as the major removal mechanism for plutonium from natural waters. This removal process is thought to affect Pu in freshwater, estuarine, and marine environments, regardless of whether its source is bomb fallout Pu, accidentally released Pu, or Pu introduced with low-level radioactive wastes (see e.g. BOWEN *et al.*, 1980). Many workers have argued that this observation is due to the interaction of the strongly hydrolyzable Pu(IV) oxidation state with the surfaces of natural particulate matter. Thermodynamic calculations, however, show that Pu(V) is the stable oxidation state in the pH range of 5 to 7 at a pE of 12 and that Pu(VI) should be the most stable oxidation state at higher pH values. Pu(IV) is predicted to be stable only below pH 5 (SANCHEZ, 1983). Recent analyses support these calculations and suggest that the dominant oxidation state of Pu in oxygenated surface waters is the oxidized Pu(V) or Pu(VI) state (e.g., NELSON and LOVETT, 1978, 1981; NELSON and ORLANDINI, 1979; BONDIETTI and TRABALKA, 1980). In such environments, Pu removal to the sediments must be explained by more than simple adsorption of the IV oxidation state.

There are few rigorous laboratory studies of the adsorption of actinides or of strongly hydrolyzable cations in general. Some of the early work on Pu focused on its interactions with soils (e.g., PROUT, 1957; RHODES, 1957). Distribution coefficient studies (e.g., DUURSMA and PARSI, 1974; GROMOV and SPITSYN, 1974; BONDIETTI *et al.*, 1976; SANCHEZ *et al.*, 1982) used water and sediments from various locations to determine the partitioning of Pu between sediment particles and water. While such studies are useful in developing predictive models for Pu distribution in a particular environment, the adsorbent and the solution phases are much too complex to provide a straightforward interpretation of the adsorption data. We choose to use simpler, better-defined experimental systems to obtain data that could be readily interpreted using adsorption equilibrium models. There have been few equivalent studies. ROZZELL and ANDELMAN (1971) characterized the sorption behavior of Pu(IV) on various silica surfaces. Clay minerals have also been used in some experiments (e.g., BONDIETTI *et al.*, 1976; DE REGGE *et al.*, 1980; BILLON, 1982).

In this paper, the results of experiments to determine the effects of pH, ionic strength, alkalinity, and dissolved organic carbon on the adsorption of Pu on goethite are presented. Two oxidation states of plutonium, Pu(IV) and Pu(V), were used in these experiments. The results of environmental studies in Saanich Inlet and Soap Lake (SANCHEZ *et al.*, in press) were used as important criteria for determining the range of the variables used in the laboratory experiments.

<sup>1</sup> School of Oceanography, University of Washington Contribution No. 1445.

ADMIN RECORD

2297

DOCUMENT CLASSIFICATION  
REVIEW WAIVER PER  
CLASSIFICATION OFFICE

SW-A-004584

Best Available Copy

## METHODS

All experiments were carried out at room temperature ( $20 \pm 2^\circ\text{C}$ ) in borosilicate glass vessels. Chemicals used were ACS analytical reagent grade. Water was distilled, demineralized and passed through 0.22  $\mu\text{m}$  Nuclepore filters prior to use in the experiments.

## A. Plutonium tracer

Two oxidation states of the isotope Pu-238 ( $t_{1/2} = 88$  yr), obtained from the Oak Ridge National Laboratory, were prepared for the experiments. The method recommended by FOTI and FREILING (1964) for the preparation of Pu(IV) and Pu(VI) was used. Briefly, Pu(IV) was prepared by first evaporating the tracer solution to dryness with hydroxylamine-HCl to reduce all Pu to the III state. The residue was then dissolved in 1 M  $\text{HNO}_3$  with a few crystals of  $\text{NaNO}_2$  added to oxidize Pu(III) to the IV state. Pu(VI) was prepared by evaporating the tracer solution to dryness with concentrated  $\text{HNO}_3$ , and dissolving the residue with 0.05 M  $\text{HClO}_4$  containing 0.005 N  $\text{K}_2\text{Cr}_2\text{O}_7$ . After adding Pu(VI) to our adsorption media, it was readily reduced to Pu(V).

The techniques of solvent extraction in TTA-xylene, lanthanum fluoride coprecipitation, adsorption on silica gel, and  $\text{CaCO}_3$  coprecipitation were used to characterize the Pu oxidation states in our tracer spike solutions and in our adsorption experiments (SANCHEZ, 1983). An organic phase containing 0.5 M 2-thenoyltrifluoroacetone (TTA) in xylene is selective for ionic Pu(IV) at pH 0.3 or lower, while the Pu(III), (V) or (VI) states are not extracted at this low pH. Lanthanum fluoride coprecipitates Pu(III), (IV) and possibly (V) but not Pu(VI). Pu(VI) adsorbs more strongly than Pu(V) on silica gel while freshly precipitated  $\text{CaCO}_3$  adsorbs Pu(V) more strongly than Pu(VI). Details of these various techniques for characterizing the oxidation states are described in FOTI and FREILING, 1964; BONDIFETI and REYNOLDS, 1976; MAGNUSSON and LACHAPPELLE, 1948; NELSON and LOVETT, 1978, and NELSON and ORLANDINI, 1979. Under the solution conditions of the adsorption experiments the oxidation states Pu(IV) and Pu(V) were confirmed to be present by a combination of these tests (SANCHEZ, 1983). Similar characteristics of these oxidation states were obtained by CHOPPIN and MORSE (in press).

## B. Adsorption

The synthetic goethite ( $\alpha\text{FeOOH}$ ) used in these experiments was prepared using the method of ATKINSON *et al.* (1967). The surface characteristics of  $\alpha\text{FeOOH}$  prepared with this procedure have been studied extensively (ATKINSON *et al.*, 1967; BALISTRERI, 1977; BALISTRERI and MURRAY, 1981, 1982).

The adsorption experiments included the following steps: (1) preparation of the solid suspension in a borosilicate glass vessel; (2) addition of the Pu tracer; (3) immediate adjustment of pH with either 0.1 N  $\text{HCl}$  or 0.1 N  $\text{NaOH}$ ; (4) equilibration of the spiked suspensions after adjusting the total volume to 20.0 ml; (5) measurement of pH prior to sampling; (6) determination of Pu partitioning between dissolved ( $<0.45 \mu\text{m}$ ) and adsorbed phases by filtering a subsample from each vessel and counting both dissolved and particulate fractions for Pu activity; and (7) oxidation state measurements for selected samples. Variations of this general procedure were used to test the effects of pH, ionic strength, carbonate alkalinity, and dissolved organic carbon on the adsorption behavior of both Pu oxidation states on  $\alpha\text{FeOOH}$ . A time series of subsamples were collected from each experimental vessel until equilibrium distribution of Pu between the soluble phase and the solid phase was attained. The goethite concentration was  $28.5 \text{ m}^2 \text{ l}^{-1}$ . A blank electrolyte solution identical to the experimental medium but containing no  $\alpha\text{FeOOH}$  was run in parallel with

the adsorption solutions to correct for adsorption on the vessels. No attempts were made to shield these experiments from light. It appears that the rates of adsorption may be different under light and dark conditions (KEENEY-KENNICUTT and MORSE, in press).

1. *Effect of pH on Pu adsorption.* Each point on the adsorption versus pH plots represents one experimental vessel. The background electrolyte was 0.1 M  $\text{NaNO}_3$ . Adsorption experiments were run using both Pu(IV) and Pu(V) initial spike solutions.

In a separate set of experiments with Pu(V), samples were collected for solvent extraction into TTA-xylene to determine if Pu(V) had been reduced to the TTA-extractable Pu(IV) state (SANCHEZ, 1983). Two series of experiments for each oxidation state (IV and V) were performed using  $1 \times 10^{-11}$  M and  $1 \times 10^{-10}$  M  $^{238}\text{Pu}$ .

2. *Effect of ionic strength on Pu adsorption.* Three different electrolytes at the following concentrations were used in these experiments: 0.1 M, 0.5 M, 1.0 M and 3.0 M  $\text{NaNO}_3$ ; 0.5 M and 3.0 M  $\text{NaCl}$ ; and 0.03 M, 0.15 M and 0.30 M  $\text{Na}_2\text{SO}_4$ . The range in ionic strengths for  $\text{NaCl}$  and  $\text{NaNO}_3$  and the sulfate concentrations were chosen to approximate values observed for Soap Lake surface and monimolimnion waters. Soap Lake is an alkaline, meromictic lake in Eastern Washington state, where we have measured relatively high concentrations of Pu compared to other natural waters (SANCHEZ, 1983). All experiments were at pH  $7.0 \pm 0.2$ .  $28.5 \text{ m}^2 \alpha\text{FeOOH l}^{-1}$ , and Pu(IV) and (V) concentrations of  $1 \times 10^{-11}$  M.

3. *Effect of carbonate alkalinity on Pu adsorption.* Appropriate volumes from a 1.0 M  $\text{NaHCO}_3$  stock solution were added to distilled, deionized water to prepare adsorption media with the following total alkalinities: 10, 30, 100, 200, 400, 500, 700, and 1000 meq/L. No attempt was made to maintain a constant ionic strength for these adsorption media and the solutions were open to the atmosphere. The pH  $8.6 \pm 0.1$  and total Pu concentration was  $10^{-11}$  M  $^{238}\text{Pu}$  (IV or V). Blanks were run along with the experiments to determine if Pu(V) was reduced to Pu(IV) in carbonate media and to correct for adsorption on the vessels. Filtered (0.22  $\mu\text{m}$ ) water from 12 m and 24 m in Soap Lake were also used to determine Pu adsorption under natural Soap Lake conditions. The anoxic sample from 24 m was left to equilibrate with air until all  $\text{Fe}^{2+}$  was oxidized prior to use in the experiments. It must be pointed out that these samples from Soap Lake may also contain potential Pu ligands, such as dissolved organic carbon, in addition to the carbonate species.

4. *Effect of dissolved organic carbon (DOC).* Two sets of experiments were performed using the naturally-occurring DOC concentrations in Soap Lake surface and monimolimnion waters. Water from 12 m and 24 m were acidified by dropwise addition of concentrated  $\text{HCl}$  until all the  $\text{CO}_2$  was removed (pH  $< 4$ ). DOC measurements for these acidified samples were done on a Dohrmann DC-80 Total Organic Carbon Analyzer system.

In the first experiment,  $^{238}\text{Pu}$  (V) tracer was added to a set of samples from 12 m at a concentration of  $1 \times 10^{-11}$  M, and the pH readjusted to pH 4 and 6 using 0.1 N  $\text{NaOH}$  solution. Filtered Soap Lake water (not degassed) from 12 m was also used as an experimental medium, with its pH constant at 9.8. An additional experimental vessel containing humic acid extract from Washington continental shelf sediments (DOC = 100 ppm, pH 9.6) was also included in this series. One ml subsamples were analysed to determine if Pu(V) was reduced to Pu(IV) in these media using solvent extraction in TTA/xylene (SANCHEZ, 1983).

A second set of experiments was conducted to determine the adsorption of  $^{238}\text{Pu}$  (IV) ( $1 \times 10^{-11}$  M) at various concentrations of DOC. Varying proportions of the acidified (pH 3.8) surface and bottom samples from Soap Lake were combined to obtain a range of DOC values. The pH was then adjusted to pH  $7.1 \pm 0.1$ . The pH was left at 7 because buffers for other pH values could complex Pu and confuse our results.

## C. Radioactivity

Liquid scintillation activity in all samples was counted in a Beckman LS 5000TD cocktail. Corp., Elk Grove Village, IL. Aqueous samples and organic samples from the mixture were adsorbed on goethite and quenched in either 0.5 M  $\text{NaOH}$  or 0.5 M  $\text{HCl}$ . A standard  $^{238}\text{Pu}$  solution was used for calibration. A Packard 4600 Spectrometer was used for counting.

## RESULTS

## 1. Kinetics of Pu

Two observations were made in the adsorption experiments: (1) the difference in the solution conditions on  $\alpha\text{FeOOH}$  is: the adsorption of Pu(IV) and Pu(V) is similar; (2) the equilibrium distribution of Pu(IV) and Pu(V) is: adsorption edge is at pH values (Figs 1 and 2).

The observed adsorption of Pu(IV) and its slow adsorption with thermodynamic data that Pu(V) is stable in the experiments (SANCHEZ, 1983) indicate that Pu(V) adsorption is reduced to the experimentally observed behavior into two Pu fractions. An organic phase indicates the presence of Pu(IV) and Pu(V).

The amount of time in the goethite experiments shown in Fig. 2, after adsorption, remained unextracted, indicating that Pu(IV) occurred in the solutions (no  $\alpha\text{FeOOH}$  into TTA-xylene this oxidation state adsorbed Pu showed xylene with time Pu(V) did not adsorb was observed. (1) Pu(IV) adsorption on goethite surface is reduced to the experimentally observed behavior into two Pu fractions. An organic phase indicates the presence of Pu(IV) and Pu(V).

### C. Radioactivity measurements

Liquid scintillation counting was used to measure the  $^{238}\text{Pu}$  activity in all samples. Ten ml of a commercially prepared counting cocktail, 3a70B, (Research Products International Corp., Elk Grove Village, Illinois) were added to 4 ml of aqueous sample adjusted to an acidity of 0.5 N HCl. For organic samples from TTA-xylene extraction, 10 ml scintillation mixture were added directly without acidification. No quenching was observed in the acid phase or the TTA-xylene organic phase, as checked with internal  $^{238}\text{Pu}$  standards prepared in either 0.5 N HCl or TTA-xylene extractant. An internal  $^{238}\text{Pu}$  standard prepared in acid solution containing goethite had showed similar counts as a standard in acid solution alone. A Packard TriCarb Model 3375 Liquid Scintillation Spectrometer was used for counting samples.

## RESULTS AND DISCUSSION

### 1. Kinetics of Pu(IV) and Pu(V) adsorption

Two observations distinguish Pu(IV) from Pu(V) adsorption on  $\alpha\text{FeOOH}$ : (1) rapid kinetics for Pu(IV) adsorption compared to Pu(V), and (2) a significant difference in their initial adsorption edges under similar solution conditions. Equilibrium adsorption for Pu(IV) on  $\alpha\text{FeOOH}$  is attained within one hour (Fig. 1a) and the adsorption edge occurs from pH 3 to 5. Under similar experimental conditions, Pu(V) does not attain equilibrium distribution even after 20 days, and the adsorption edge gradually shifts from pH 7 to lower pH values (Figs. 1b and 1c).

The observed shift in the adsorption edge for Pu(V) and its slow adsorption kinetics appear to be inconsistent with thermodynamic calculations which predict that Pu(V) is stable under the conditions of these experiments (SANCHEZ, 1983). The gradual increase in Pu(V) adsorption with time, caused its adsorption edge to approach that for Pu(IV), suggesting that Pu(V) may be reduced to the lower oxidation state. This was tested experimentally by investigating the solvent extraction behavior into TTA/xylene of the adsorbed and soluble Pu fractions. Any significant removal of Pu into the organic phase under the low pH extraction conditions indicates the presence of the Pu(IV) oxidation state.

The amount of TTA-extractable Pu as a function of time in the adsorbed and the soluble fractions of goethite experiments spiked initially with Pu(V) is shown in Fig 2. The initial time points are for 1 hour after adsorption. The data show that soluble Pu remained unextracted (<5%) into TTA-xylene with time, indicating that no significant reduction of Pu(V) to Pu(IV) occurred in solution. This observation is further supported by TTA analyses of corresponding blank solutions (no  $\alpha\text{FeOOH}$  added), where no extraction into TTA-xylene was found. Thus, Pu(V) remained as this oxidation state in solution. In contrast, the goethite-adsorbed Pu showed increasing extraction into TTA-xylene with time. However, at the low pH (<3.8) where Pu(V) did not adsorb, no extraction into the TTA phase was observed. These observations suggest two possibilities: (1) Pu(V) is reduced to Pu(IV) following its adsorption on goethite, or (2) Pu(V) close to the goethite surface is reduced to Pu(IV), with the Pu(IV) sub-

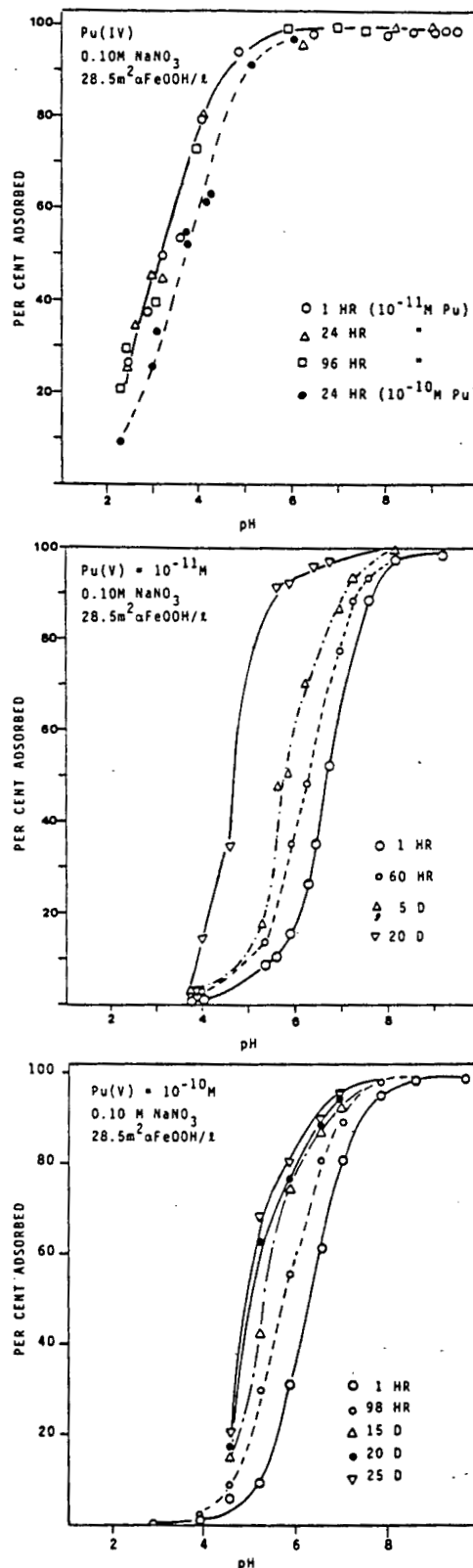


FIG. 1. a) Adsorption of Pu(IV) on goethite as a function of pH from 0.1 M  $\text{NaNO}_3$  solution at two plutonium concentrations ( $10^{-11}$  and  $10^{-10}$  M). b) The adsorption of Pu(V) on goethite as a function of pH from 0.10 M  $\text{NaNO}_3$  solution at  $10^{-11}$  M. c) Adsorption of Pu(V) on goethite as a function of pH from 0.10 M  $\text{NaNO}_3$  solution at  $10^{-10}$  M.

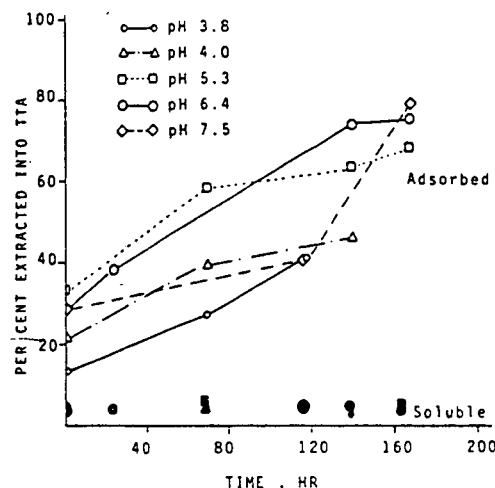


FIG. 2. The percent of total Pu(V) added that became TTA-extractable Pu(IV) as a function of time in the adsorbed and the dissolved fractions. Results from goethite experiments initially spiked with Pu(V). Initial data points are for 1 hour after adsorption started. Error for TTA extraction is  $\pm 5\%$ .

sequently rapidly adsorbed. The data are not sufficient to distinguish which of these two mechanisms is occurring. However, recent observations of KEENEY-KENNICUTT and MORSE (1985) indicate that Pu(V) adsorbs as this oxidation state on a variety of mineral surfaces. Their results would support the first mechanism to account for our observations, particularly since we found that no reduction occurs when Pu(V) is not adsorbed.

Three possibilities may be suggested to account for the observed reduction of Pu(V) after adsorption: (1) thermodynamic data are wrong and Pu(IV) is the stable form under the pH conditions of our experiments (pH 5 to 7); (2) trace amounts of reducing agents are present on the goethite surface; or (3) the reduction of Pu(V) occurs via a radiolysis or disproportionation reaction. If Pu(IV) is really the stable oxidation state the implication is that Pu(V) is reduced slowly by water when it is immobilized by adsorption. Pu(V) in homogeneous solutions is kinetically stable and is not reduced for indefinite time periods. It was not possible to determine the presence of trace amounts of reducing agents in the experiments. Given the small concentrations of Pu used, however, it is conceivable that any trace constituent occurring as an impurity in the media may potentially act as a reducing agent. There is the more unlikely possibility that as soon as the radioactivity becomes concentrated on the solid surface, the production of reducing agents such as  $H_2O_2$ , OH radicals and nitrite (MINER and SEED, 1967) via the radiolysis mechanism becomes important. The concentrations of these species would probably be too small to be detected because of the minimal radioactivity in the experiments. The final possibility is the reduction of Pu(V) via the disproportionation reaction, whereby

Pu(IV) and Pu(VI) species are produced (CONNICK, 1949; RABIDEAU, 1957). KEENEY-KENNICUTT and MORSE (in press) invoked this mechanism to account for the reduction of Pu(V) to Pu(IV) in their goethite adsorption experiments.

## 2. Effect of pH on Pu(IV) and Pu(V) adsorption

The major difference between the adsorption of Pu(IV) and Pu(V) is in the position of their initial pH adsorption edges under similar solution conditions ( $I = 0.1$  M  $NaNO_3$ ). In Fig. 1a, the adsorption edge for Pu(IV) occurs at the pH range 3 to 4, in contrast to that for Pu(V) (Figs. 1b and 1c), which has an initial adsorption edge between pH 6 to 7. The pH of the adsorption edge for Pu(V) is a lower limit because of the uncertain role of Pu(V) reduction to Pu(IV). The one hour data are probably a close approximation.

The difference in the adsorption edge is possibly linked to the tendency of these ions to hydrolyze in solution. BALISTRERI *et al.* (1981) found a linear correlation between the apparent adsorption equilibrium constant for metal adsorption on goethite and the hydrolysis constants of that specific metal ion. The larger the hydrolysis constant, the stronger the adsorption and the lower the pH of the adsorption edge. Pu(IV) (in the ionic form  $Pu^{4+}$ ) is the most strongly hydrolyzed and Pu(V) (as  $PuO_2^+$  ion) the least hydrolyzed among the common oxidation states of Pu in aqueous solutions. The observed difference in their initial adsorption edges is therefore consistent with their different hydrolytic character.

Another observation is the shift in the adsorption edges to slightly higher pH range with increased Pu concentration for each oxidation state (Figs. 1a, b, and c). This is similar to the results of BALISTRERI and MURRAY (1982) for Cu, Pb, Zn, and Cd adsorption on goethite as a function of the metal concentration and may be due to strong binding site limitation. This suggests that adsorption of Pu rather than its precipitation on the goethite surface is the controlling mechanism.

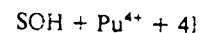
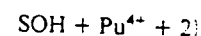
We proceeded to model the adsorption versus pH data. We first determined adsorption equilibrium constants to enable us to predict Pu adsorption in different environments. The same constants are used later to estimate the values of dissolved Pu-carbonate complexes.

In recent years, several electrostatic models have been developed for describing ion adsorption at the oxide/water interface (see WESTALL and HOHL, 1980, for a review of these various models). Our adsorption experiments on goethite were designed so that the results could be interpreted using the site-binding or triple layer model. This model has already been successfully applied by BALISTRERI and MURRAY (1981, 1982) for the adsorption of major ions and trace metals on goethite and this was the main reason it was used in this study. Other models exist that would also fit the data

equally well. This sorption data using (WESTALL *et al.*, 1981).

The details of the theoretical and experimental surface, will not be referred to YATES *et al.* (1981) for details. The model assumes a structure can be described by a physical parameter have presented the goethite interaction. Their model parameters: number of surface capacitances, the surface and the surface  $CO_3$  are used here.

Modelling the Pu pH involves defining constants for Pu in Four reactions involving hydrolysis species were of Pu(IV).



In these equations, the  $K^{INT}$  is the intrinsic association with goethite that were required to  $-2.00$   $-5.90$  and  $Pu(OH)_2^+$  and  $Pu(OH)_3$  addition of these constants is shown in Fig. 3. The  $K^{INT}$  of each reaction on goethite. The values are a unit  $0.5$  log units. The  $K^{INT}$  reported by METIVIER (1981) used in these calculations (CHOPPIN, 1983). At pH 4, the  $K^{INT}$  obtained at slightly higher pH. No corrections were made to the model calculations. The  $K^{INT}$  are still some uncertainty for Pu(IV) and the hydrolysis constants. The uncertainties are no general conclusions. The data for Pu(V) NEQL modelling was not attained. It remained stable in the

produced (CONNICK, KENEY-KENNICUTT and mechanism to account Pu(IV) in their goethite

### Pu(V) adsorption

between the adsorption of Pu(IV) and Pu(V) at different pH and solution conditions ( $I = 0.1$  M NaNO<sub>3</sub>) is shown in Fig. 2. The adsorption edge for Pu(IV) is at pH 3 to 4, in contrast to Pu(V), which has an initial adsorption edge at pH 6 to 7. The pH of the adsorption edge for Pu(V) is lower than that for Pu(IV) because of the lower limit because of the reduction to Pu(IV). The close approximation of the adsorption edge is possibly due to the fact that Pu(V) ions tend to hydrolyze in solution (MURRAY, 1981) found a linear correlation between Pu adsorption equilibrium on goethite and the hydrolysis constant of the metal ion. The larger the hydrolysis constant, the stronger the adsorption on goethite. Pu(IV) is a weakly hydrolyzed species, while Pu(V) is a strongly hydrolyzed species. Pu(V) is the most strongly hydrolyzed among the actinides. Pu(V) is the most strongly hydrolyzed among the actinides.

shift in the adsorption edge with increased Pu concentration (Figs. 1a, b, and c) is of BALISTRERI and MURRAY (1981) and BALISTRERI and MURRAY (1981) and Cd adsorption on goethite. The metal concentration is not a limiting factor in this case. This is rather than its precipitation, the controlling mechanism.

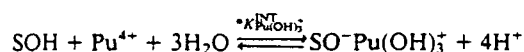
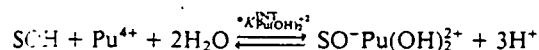
adsorption versus pH for Pu(IV) and Pu(V) at different solution conditions. The adsorption equilibrium constants for Pu(IV) and Pu(V) are used later to model Pu-carbonate complexes.

thermodynamic models have been used to model ion adsorption at the goethite surface (BALISTRERI and HOHL, 1980, 1981, 1982). Our adsorption data are designed so that the results can be compared with the site-binding or triple site-binding model. BALISTRERI and MURRAY (1981, 1982) for Pu(IV) and Pu(V) on goethite. Our adsorption data for trace metals on goethite were used in this study. It would also fit the data

equally well. This model was applied to our Pu adsorption data using the MINEQL computer program (WESTALL *et al.*, 1976).

The details of the site-binding model, and the theoretical and experimental work that went into deriving the various parameters used to describe the goethite surface, will not be discussed here. The reader is referred to YATES *et al.* (1974), DAVIS *et al.* (1978), WESTALL and HOHL (1980), and BALISTRERI and MURRAY (1981) for details. Briefly, the site-binding model assumes a structure of the electrical double layer which can be described mathematically by a set of adjustable physical parameters. BALISTRERI and MURRAY (1981) have presented the experimental data used for defining goethite interactions in simple electrolyte systems. Their model parameters for the surface area, the total number of surface sites, the inner and outer layer capacitances, the surface hydrolysis constants of goethite and the surface complexation constants for Na<sup>+</sup> and NO<sub>3</sub><sup>-</sup> are used here.

Modelling the Pu adsorption data as a function of pH involves defining the intrinsic surface complexation constants for Pu interaction with the goethite surface. Four reactions involving the adsorption of Pu(IV) hydrolysis species were required to describe the adsorption of Pu(IV).



In these equations, SOH represents a surface site, and the  $*K^{\text{INT}}$  is the intrinsic constant describing Pu association with goethite. The values of the log  $*K^{\text{INT}}$  that were required to fit the adsorption data were 2.50, -2.00, -5.90 and -12.0 for Pu(OH)<sup>3+</sup>, Pu(OH)<sup>2+</sup>, Pu(OH)<sup>+</sup> and Pu(OH)<sup>0</sup> respectively. The incremental addition of these constants to produce a model best fit is shown in Fig. 3. In this way the effect of the addition of each reaction on the final model curve can be seen. The values are a unique set and are accurate to at least 0.5 log units. The hydrolysis constants for Pu(IV) reported by METIVIER and GUILLAUMONT (1976) were used in these calculations. (BAES and MESMER, 1976; CHOPPIN, 1983). Although these constants were obtained at slightly higher ionic strengths ( $I = 1.0$  M), no corrections were made for ionic strength in our model calculations. It should be clearly stated that there are still some uncertainties in the hydrolysis constants for Pu(IV) and the values for  $*K^{\text{INT}}$  depend on the hydrolysis constants used in the calculations. These uncertainties are not large enough to invalidate our general conclusions.

The data for Pu(V) were not interpreted using MINEQL modelling because an equilibrium distribution was not attained. It was uncertain whether Pu(V) remained stable in the experiments. In addition, the hydrolysis constants for Pu(V) are even less well known than those for Pu(IV).

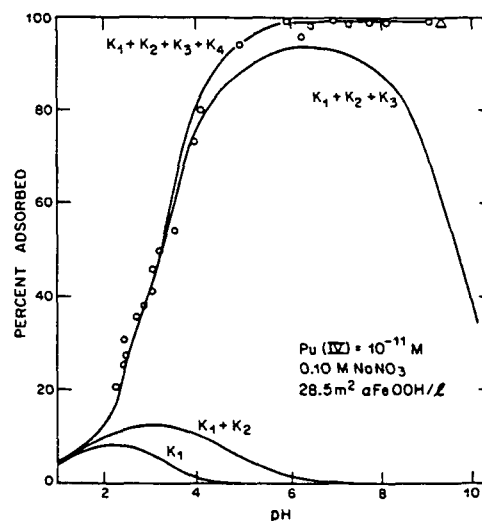


FIG. 3. Adsorption of Pu as a function of pH on goethite. Four reactions for the adsorption of Pu(IV) hydrolysis species are required to model the data (circles). The incremental addition of these reactions to the equilibrium program MINEQL to produce a model best fit is shown.

hydrolysis constants for Pu(V) are even less well known than those for Pu(IV).

### 3. Effect of ionic strength on Pu adsorption

Changes in ionic strength do not appear to exert a major control on the adsorption of either Pu(IV) or Pu(V). The adsorption of <sup>238</sup>Pu(IV) and <sup>238</sup>Pu(V) on  $\alpha$ -FeOOH did not vary with increasing ionic strength (up to  $I = 3$ ) at pH  $7.0 \pm 0.2$ , regardless of the background electrolyte. As summarized in Table 1, greater than 90% of the total activity for both oxidation states is found on the goethite phase after equilibrium distribution is attained. Sulfate ion did not influence adsorption of either Pu(IV) or Pu(V) up to 0.3 M SO<sub>4</sub><sup>2-</sup> although it is one of the known complexing agents for Pu (CLEVELAND, 1979). Enhancement of Pu adsorption due to SO<sub>4</sub><sup>2-</sup> as seen for Cu and Zn adsorption on goethite (BALISTRERI and MURRAY, 1982) could not be identified in these experiments because we were in the greater than 90% adsorption range.

### 4. Effect of carbonate alkalinity

The adsorption of <sup>238</sup>Pu(IV) and <sup>238</sup>Pu(V) on  $\alpha$ -FeOOH as a function of increasing alkalinity is plotted in Figs. 4a and 4b. The experiments were open to the atmosphere. The pH values for the individual vessels were constant at about pH  $8.60 \pm 0.10$  during the course of the experiments. The lower curve in each plot represents adsorption data after 1 hour of equilibration; the upper curve is for the "true" equilibrium adsorption points (96 hours for Pu(IV) and ~300 hours for Pu(V)). Adsorption of both oxidation states is unaffected by alkalinity values less than about 100 meq/



Table 1. Adsorption of  $^{238}\text{Pu(IV)}$  and V on  $\alpha\text{FeOOH}$  as a function of ionic strength. pH  $7.0 \pm 0.2$ ,  $\text{Pu}_{\text{total}} = 1 \times 10^{-11} \text{ M}$ .

Electrolyte Solution	Oxidation States	% Adsorbed at Equilibrium
0.1 M $\text{NaNO}_3$	IV V	97 $\pm$ 3 93 $\pm$ 3
0.5 M $\text{NaNO}_3$	IV V	97 $\pm$ 3 92 $\pm$ 3
1.0 M $\text{NaNO}_3$	IV V	98 $\pm$ 3 97 $\pm$ 3
3.0 M $\text{NaNO}_3$	IV V	98 $\pm$ 3 93 $\pm$ 3
0.5 M $\text{NaCl}$	IV V	96 $\pm$ 3 96 $\pm$ 3
3.0 M $\text{NaCl}$	IV V	97 $\pm$ 3 97 $\pm$ 3
0.03 M $\text{Na}_2\text{SO}_4$	IV V	97 $\pm$ 3 93 $\pm$ 3
0.15 M $\text{Na}_2\text{SO}_4$	IV V	97 $\pm$ 3 95 $\pm$ 3
0.30 M $\text{Na}_2\text{SO}_4$	IV V	95 $\pm$ 3 93 $\pm$ 3

L, where the amount adsorbed on  $\alpha\text{FeOOH}$  is similar to that obtained at the same pH in 0.1 M  $\text{NaNO}_3$  solution. The effect of alkalinity, however, becomes progressively more important for alkalinity values greater than 100 meq/L. and adsorption is totally inhibited at a concentration of 1000 meq/L. The adsorption from natural filtered Soap Lake water at alkalinities of 144 meq/L (pH = 9.8) and  $\sim 1200$  meq/L (pH = 9.5) are shown in the same plots. At equilibrium, the amounts of Pu IV and V adsorbed onto goethite in these Soap Lake media agree with the expected removal based on alkalinity alone. However, it must be pointed out that the filtered Soap Lake water contains potential Pu ligands other than the carbonate species, such as dissolved organic carbon, that may also influence Pu adsorption behavior. The effects of organic carbon will be discussed later.

At equilibrium, the adsorption *versus* alkalinity plots for both Pu(IV) and Pu(V) overlap (Figs. 4a and 4b). This suggests that either the adsorption behavior of Pu(IV) and Pu(V) under high carbonate concentrations are similar or that there is a redox transformation of one oxidation state to another. To test this hypothesis, solutions of both Pu(IV) and (V) in high carbonate media in the absence of solid were taken for solvent extraction with TTA-xylene.

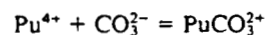
The Pu(IV) tracer in 1.0 M  $\text{NaHCO}_3$ , at pH 8.6 in the absence of  $\alpha\text{FeOOH}$ , remained in the soluble ( $<0.45 \mu\text{m}$ ) fraction but only 50% of the total activity in solution could be extracted into TTA after 300 hours (Table 2). This observation suggests that although Pu(IV) remained filterable, only 50% was in the ionic form which can be extracted into TTA. In a less concentrated carbonate medium (0.03 M  $\text{NaHCO}_3$ , pH 8.6), increasing amounts of non-extractable Pu ( $<0.45 \mu\text{m}$ ), presumably polymeric species of Pu(IV), were

found with time. This suggests that hydrolysis is important in this medium and that carbonate complexing can not compete effectively with the formation of hydrolytic Pu(IV) species. BONDIETTI *et al.* (1976) observed that polymeric Pu was formed and adsorbed to the walls of the reaction vessel in 0.1 M  $\text{NaHCO}_3$  solution at pH 8.0. At the Pu concentration ( $\sim 10^{-8}$  M) which they used in their experiments, they concluded that carbonate ions are unable to stabilize a Pu(IV) monomeric complex.

Similar tests with the Pu(V) oxidation state showed that it remained soluble and did not extract significantly into TTA in either the 1.0 M  $\text{NaHCO}_3$  or the 0.03 M  $\text{NaHCO}_3$  blank solutions (no goethite present) (Table 2). Pu(V) appeared to be stable in this oxidation state at these solution conditions. In the presence of  $\alpha\text{FeOOH}$ , the amount of TTA-extractable Pu in the soluble fraction increased with time. In one experiment (1.0 M  $\text{NaHCO}_3$ , pH 8.6), to which Pu(V) was initially added, only 2 to 4% of the total Pu adsorbed and 93% of the soluble fraction was extracted into TTA after 300 hours (Table 2). These observations indicate that in the presence of the adsorptive surface, Pu(V) is reduced to Pu(IV). This reduction was also observed in the pH experiments but in that case, Pu(IV) remained on the solid. Here, it appears that the complexation of Pu(IV) by carbonate ligands removes the adsorbed Pu. This provides further evidence that Pu(V) reduction occurs in the presence of goethite. Thus, the similarity in the sorption plots for Pu(IV) and Pu(V) *versus* increasing alkalinity is due to the reduction of Pu(V) to Pu(IV) in the presence of the oxide surface followed by complexation with carbonate ions.

In the carbonate experiments, three possible factors are likely to be influencing the Pu distribution: (1) adsorption onto the goethite surface, (2) hydrolysis of Pu, and (3) carbonate complexing. We have attempted a preliminary interpretation of our data using the site-binding model including all three interactions. In the preceding section, an adsorption model that sufficiently described the adsorption behavior of Pu(IV) as a function of pH was developed. An extension of this model to include carbonate complexing was then carried out. We will show here how the formation of such complexes could possibly influence the adsorption of Pu(IV). This model can be refined as the thermodynamic data is improved.

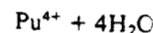
The formation of dissolved Pu(IV)- $\text{CO}_3$  complexes is poorly understood (CLEVELAND, 1979; KIM *et al.*, 1983). MOSKVIN and GEL'MAN (1958) attempted to determine the formation constants for Pu(IV)- $\text{CO}_3$  complexes by measuring the solubility of  $\text{Pu(OH)}_4$  (am) at pH 11.5 in concentrated  $\text{K}_2\text{CO}_3$  solutions. They assumed that the complex  $\text{PuCO}_3^{2+}$  was formed by the reaction:



and estimated the formation constant to vary from  $10^{34}$  to  $10^{42}$ . SCHWAB and FELMY (1983) reviewed this

FIG. 4.  
carbonate  
also show

data set and prop  
a mixed hydrox  
reaction:



with log  $K = -4$ .  
istry point of vi  
unlikely. A third  
is that a  $\text{CO}_3^{2-}$  liq  
 $\text{Pu(OH)}_3\text{CO}_3^-$ . Th  
 $\text{Pu(OH)}_4\text{CO}_3^{2-}$  as  
model and tested  
summed that the ca  
of goethite as des  
(1982):

6

that hydrolysis is im-  
carbonate complexing  
the formation of hy-  
ETTI *et al.* (1976) ob-  
med and adsorbed to  
n 0.1 M NaHCO<sub>3</sub> so-  
centration ( $\sim 10^{-8}$  M)  
ments, they concluded  
to stabilize a Pu(IV)

oxidation state showed  
ot extract significantly  
HCO<sub>3</sub> or the 0.03 M  
ethite present) (Table  
on this oxidation state

In the presence of  
extractable Pu in the  
ne. In one experiment  
ch Pu(V) was initially  
Pu adsorbed and 93%  
acted into TTA after  
ervations indicate that  
e surface. Pu(V) is re-  
was also observed in  
ase, Pu(IV) remained  
at the complexation of  
oves the adsorbed Pu.  
that Pu(V) reduction  
e. Thus, the similarity  
and Pu(V) *versus* in-  
reduction of Pu(V) to  
xide surface followed  
ions.

three possible factors  
Pu distribution: (1) ad-  
ace, (2) hydrolysis of  
g. We have attempted  
our data using the site-  
ee interactions. In the  
model that sufficiently  
or of Pu(IV) as a func-  
tension of this model  
was then carried out.  
imation of such com-  
ce the adsorption of  
ned as the thermody-

Pu(IV)-CO<sub>3</sub> complexes  
ND, 1979; KIM *et al.*  
(1958) attempted to  
stants for Pu(IV)-CO<sub>3</sub>  
bility of Pu(OH)<sub>4</sub>(am)  
O<sub>3</sub> solutions. They as-  
<sub>3</sub><sup>2+</sup> was formed by the

PuCO<sub>3</sub><sup>2+</sup>

constant to vary from  
Y (1983) reviewed this

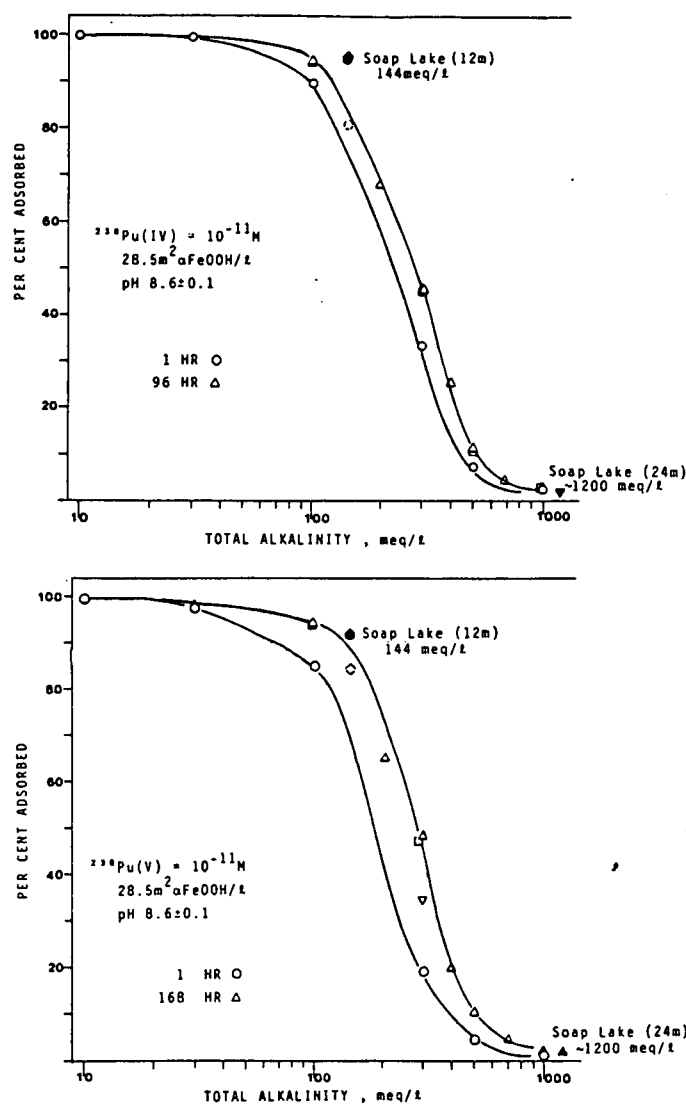
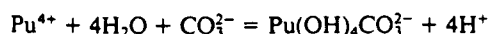
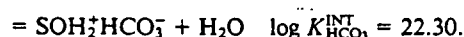
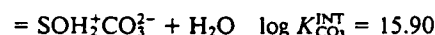


FIG. 4. a) The effect of carbonate alkalinity on the adsorption of Pu(IV) on goethite. b) The effect of carbonate alkalinity on the adsorption of Pu(V) on goethite. Adsorption from natural Soap Lake water is also shown. (Solid symbols).

data set and proposed that the main species is probably a mixed hydroxy-carbonate complex formed by the reaction:



with  $\log K = -4.1 \pm 1.0$ . From a coordination chemistry point of view the species  $\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$  seems unlikely. A third possibility that has not been explored is that a  $\text{CO}_3^{2-}$  ligand could replace one  $\text{OH}^-$  to form  $\text{Pu}(\text{OH})_3\text{CO}_3^-$ . The formation of the species  $\text{PuCO}_3^{2+}$ ,  $\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$  and  $\text{Pu}(\text{OH})_3\text{CO}_3^-$  were added to the model and tested using MINEQL. In addition we assumed that the carbonate ions interact with the surface of goethite as described by BALISTRERI and MURRAY (1982):



We also assumed that the intrinsic adsorption constants derived previously for Pu(IV)-goethite interaction are still valid.

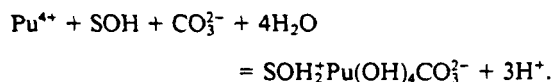
In our first calculations we assumed that a Pu(IV)-CO<sub>3</sub> complex forms and that these species do not adsorb. The formation of either  $\text{PuCO}_3^{2+}$  or  $\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$  with the formation constants cited above would result in no adsorption under the conditions of our experiments (curve A). This model is clearly inconsistent with our experimental data (curve

Table 2. Characteristics of Pu(IV) and (V) tracers in NaHCO<sub>3</sub> solution. Pu<sub>total</sub> = 10<sup>-11</sup> M.

Oxidation state	NaHCO <sub>3</sub> , M	pH	Method	Results
Pu(IV)	1.0 M	8.6	TTA extraction	filterable through 0.45 μm filter 50% in TTA
Pu(IV)	0.03 M	8.6		15% retained on 0.45 μm filter after 24 hr.
Pu(V)	1.0 M	8.6	TTA extraction	filterable through 0.45 μm filter 2% in TTA
Pu(V)	0.03 M	8.6	TTA extraction	filterable through 0.45 μm filter 3% in TTA
Pu(V)	0.03 M	8.6 with αFeOOH	TTA extraction of soluble fraction	87% in TTA after 100 hr.
Pu(V)	1.0 M	8.6 with αFeOOH	TTA extraction of soluble fraction	93% in TTA after 300 hr.

D). We then tested the possibility that the formation constants are too large. We varied the formation constants until the % adsorbed was about 50% at an alkalinity of 300 meq l<sup>-1</sup>. Then we varied the alkalinity to generate the curve. Because the formation of each of the three species considered involves only one CO<sub>3</sub><sup>2-</sup>, the effect of all three species is the same (curve B). The log formation constants for PuCO<sub>3</sub><sup>+</sup>, Pu(OH)<sub>4</sub>CO<sub>3</sub><sup>2-</sup> and Pu(OH)<sub>3</sub>CO<sub>3</sub><sup>-</sup> would have to be +27.2, -7.1, and +1.40 respectively. The formation constants for PuCO<sub>3</sub><sup>+</sup> and Pu(OH)<sub>4</sub>CO<sub>3</sub><sup>2-</sup> would be weaker than those previously estimated. Regardless of whether these are reasonable constants the formation of these species would not result in a steep enough dependency of % adsorbed on alkalinity. Adding complexes with two or more carbonate ligands (e.g., Pu(CO<sub>3</sub>)<sub>2</sub>) would make the curve steeper.

We also tested what the distribution would look like if the dissolved Pu(OH)<sub>4</sub>CO<sub>3</sub><sup>2-</sup> species could adsorb. SCHINDLER (1981) reviewed some of the experimental evidence for the formation of "ternary surface complexes" (i.e., complexes that participate in a surface reaction) and suggested that these complexes should not be ignored in model calculations which consider the effects of dissolved ligands. We assumed that the formation constant for Pu(OH)<sub>4</sub>CO<sub>3</sub><sup>2-</sup> is accurate and that this species adsorbs on the surface of goethite according to:



The curve C in Fig. 5 corresponds to this example with an intrinsic adsorption constant of  $\log K_{\text{Pu}(\text{OH})_4\text{CO}_3^{2-}}^{\text{INT}} = 15.6$ . The alkalinity dependency of this curve is a much closer representation of the experimental data.

Though there are some uncertainties in the adsorption models one point is clear and that is that increasing

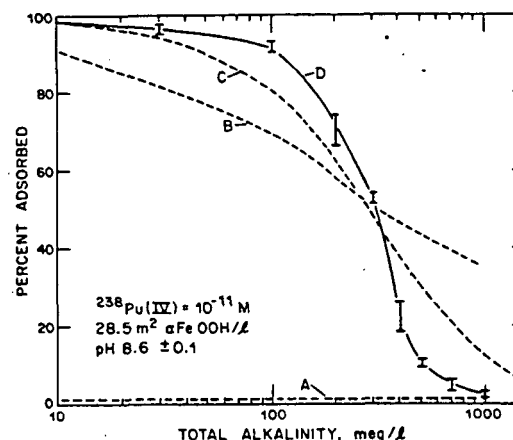


FIG. 5. Adsorption equilibrium model fits to adsorption versus alkalinity data (curve D) of Pu(IV) on goethite. The curves represent the following conditions. a) Formation constant for Pu(OH)<sub>4</sub>CO<sub>3</sub><sup>2-</sup> is  $\log K = -4.1$  or for PuCO<sub>3</sub><sup>+</sup> is  $\log K = 34$ . b) Formation constant for Pu(OH)<sub>4</sub>CO<sub>3</sub><sup>2-</sup> is  $\log K = -7.2$  or for Pu(OH)<sub>3</sub>CO<sub>3</sub><sup>-</sup> is  $\log K = +1.40$  or for PuCO<sub>3</sub><sup>+</sup> is  $\log K = +27.2$ . c) Formation constant for Pu(OH)<sub>4</sub>CO<sub>3</sub><sup>2-</sup> is  $\log K = -4.1$  and the adsorption equilibrium constant for Pu(OH)<sub>4</sub>CO<sub>3</sub><sup>2-</sup> is  $\log K = 15.6$ .

alkalinity above 100 meq l<sup>-1</sup> can decrease the adsorption of Pu(IV) and Pu(V). This appears to be due to the formation of Pu-CO<sub>3</sub> complexes. Model profiles suggest that the best fit to the data will be when Pu-CO<sub>3</sub> complexes form and then form a ternary complex with the goethite surface.

##### 5. Effect of dissolved organic carbon (DOC) on Pu adsorption

The naturally-occurring DOC in Soap Lake water reduced Pu(V) to the IV oxidation state, as indicated

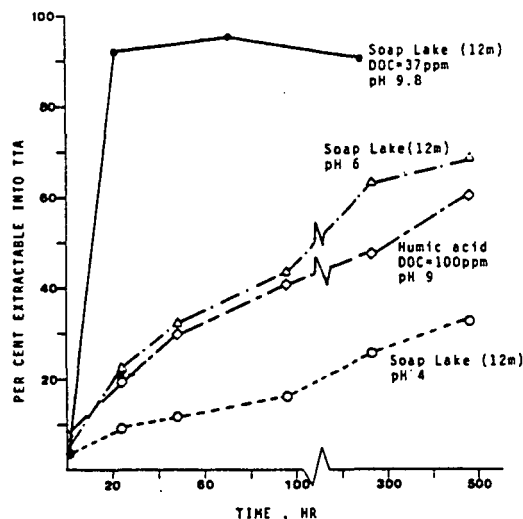


FIG. 6. The kinetics of Pu(V) reduction to TTA extractable Pu(IV) in Soap Lake water samples containing the naturally-occurring dissolved organic carbon fraction in the lake water. Humic acid extract is used as a reference organic material.

by its increased (Fig. 6). The rate pH, and was far sample at pH 9. ington continen: reduce Pu(V) (Fi obtained by NA: by humic acids i. observations agr *et al.* (1976) that to Pu(IV) in the thermore, the re: face waters sho: agreement with (1978) that Pu(I: eutrophic waters

Since DOC w of DOC on Pu a IV oxidation st: these experimen: equilibrium ads: ements, and (2) a creasing DOC co: to results of NE: that the distrib: iments and wat: increased.

A simple matl developed for th also applied to th calculations are (1984). Essential: two different bi: ALBERTS *et al.* interactions reas:

One major diff and those obtain: concentrations is th:

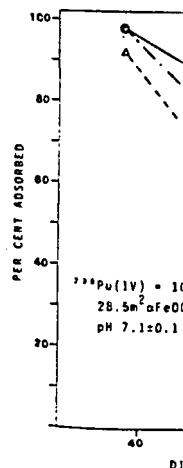


FIG. 7. The effect of Soap Lake waters on the alkalinity was zero.



by its increased extraction into TTA/xylene with time (Fig. 6). The rate of reduction increased with increasing pH, and was fastest in the non-degassed Soap Lake sample at pH 9.8. A humic acid extract from Washington continental shelf sediments was also found to reduce Pu(V) (Fig. 6). These results are similar to those obtained by NASH *et al.* (1981) for Pu(VI) reduction by humic acids in  $\text{NaHCO}_3$  solution. These laboratory observations agree with the suggestion of BONDIETTI *et al.* (1976) that Pu(V) should be unstable to reduction to Pu(IV) in the presence of organic substances. Furthermore, the results suggest that Pu in Soap Lake surface waters should be in the IV oxidation state, in agreement with the observation of WAHLGREN *et al.* (1978) that Pu(IV) is the dominant oxidation state in eutrophic waters.

Since DOC was found to reduce Pu(V), the effect of DOC on Pu adsorption was studied using only the IV oxidation state. Two observations were noted in these experiments: (1) a much slower approach to equilibrium adsorption compared to the pH experiments, and (2) a slight decrease in adsorption with increasing DOC concentration (Fig. 7). These are similar to results of NELSON *et al.* (1980, 1981), who found that the distribution coefficient for  $^{237}\text{Pu}$  between sediments and water decreased as the DOC concentration increased.

A simple mathematical model similar to the one we developed for the Pu-goethite-carbonate system was also applied to the adsorption data. The results of our calculations are published elsewhere (SIBLEY *et al.*, 1984). Essentially, we found that a model assuming two different binding sites on DOC as suggested by ALBERTS *et al.* (1980) and neglecting DOC-goethite interactions reasonably fit the adsorption data.

One major difference between these adsorption data and those obtained at increasing carbonate ion concentrations is that even at the high DOC concentrations

for Soap Lake monimolimnion waters (DOC = 220 ppm), a substantial fraction (70%) of Pu(IV) still adsorbs on goethite. In this same water with greater than 1 M total carbonate concentration, no adsorption on goethite was obtained. These results suggest that carbonate anions inhibit Pu(IV) adsorption on goethite more strongly than DOC at the concentration ranges tested for these ligands. SIMPSON *et al.* (1980) reached a similar conclusion for Mono Lake.

## CONCLUSIONS

1. Under similar solution conditions, the adsorption edge for Pu(IV) occurs at a significantly lower pH range (pH 3 to 5) than for Pu(V) (initially at pH 5 to 7). This result is consistent with the different hydrolytic character of these two oxidation states in aqueous solutions.

2. For Pu(V), a gradual shift in the adsorption edge to lower pH ranges occurs with increasing time of adsorption. Solvent extraction tests with TTA/xylene indicate that the adsorbed Pu(V) has been reduced to the IV oxidation state. Although thermodynamic calculations predict that Pu(V) is stable under the solution conditions of the experiments, it appears that it is unstable to reduction to Pu(IV) in the presence of an adsorptive surface.

3. The triple layer model for the adsorption of Pu(IV) on goethite in  $\text{NaNO}_3$  predicts that four hydrolytic species of Pu(IV),  $\text{Pu}(\text{OH})^{3+}$ ,  $\text{Pu}(\text{OH})_2^{2+}$ ,  $\text{Pu}(\text{OH})_3^+$  and  $\text{Pu}(\text{OH})_4^0$  adsorb on the goethite surface. The log intrinsic constants for the interaction of these species with the oxide surface that reasonably fit the adsorption data are 2.50, -2.0, -5.9 and -12.0, respectively. Since Pu(V) was unstable in the presence of goethite, the data were not used in the triple layer model calculations.

4. An increase in ionic strength from 0.1 M to 3.0 M  $\text{NaNO}_3$  or  $\text{NaCl}$  did not affect the adsorption of Pu on goethite. Sulfate (0.03 M to 0.3 M) also did not decrease Pu removal on goethite although it is one of the known inorganic complexers for Pu.

5. Pu(V) was reduced to Pu(IV) in solution in the presence of natural dissolved organic carbon (DOC) from Soap Lake. At 240 ppm DOC concentration, Pu(IV) adsorption on goethite was reduced by 30%.

6. Increasing concentrations of carbonate ions decreased Pu(IV) and Pu(V) adsorption on goethite. At a concentration of 1 M  $\text{NaHCO}_3$  (pH 8.6) Pu adsorption was inhibited completely. The decrease in adsorption appears due to formation of a  $\text{Pu-CO}_3$  complex, however, the value of the formation constant is poorly known and it is also uncertain whether or not the complex adsorbs.

**Acknowledgements**—This manuscript benefited greatly from discussions and comments from P. Santschi, R. Anderson, L. Balistrieri, B. Honeyman, R. McDuff and L. Miller. Dr. W. R. Schell helped with the initial aspects of the senior author's study. L. Miller and J. I. Murray helped collect the

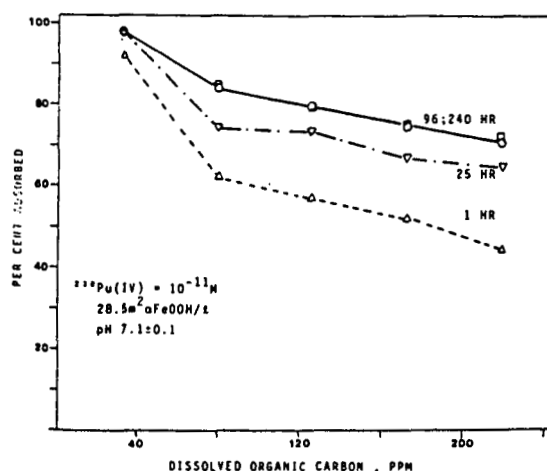


FIG. 7. The effect of dissolved organic carbon from Soap Lake waters on the adsorption of Pu(IV) on goethite. The alkalinity was zero in these experiments.

Soap Lake samples. T. Rasp typed the manuscript. This research was funded by NSF OCE 82-14072.

Editorial handling: E. R. Sholkovitz

## REFERENCES

- ALBERTS J. J., LUTKENHOFF D., GEIGER R. A. and GANT D. (1980) Stability constants determined for complexes of  $^{233}\text{U}$ ,  $^{237}\text{Pu}$ ,  $^{237}\text{Np}$  and  $^{99}\text{Tc}$  with natural stream organic material. In *Savannah River Ecology Laboratory, University of Georgia, Annual Report 1980*.
- ATKINSON R. J., POSNER A. M. and QUIRK J. P. (1967) Adsorption of potential-determining ions at the ferric oxide-aqueous electrolyte interface. *J. Phys. Chem.* **71**, 550-558.
- BAES S. F. and MESMER R. E. (1976) *The Hydrolysis of Cations*. Wiley-Interscience, 489 pp.
- BALISTRIERI L. S. (1977) *The basic surface characteristics of goethite ( $\alpha\text{FeOOH}$ )*. M.S. thesis, University of Washington, Seattle.
- BALISTRIERI L. S. and MURRAY J. W. (1981) The surface chemistry of goethite ( $\alpha\text{FeOOH}$ ) in major ion seawater. *Amer. J. Sci.* **281**, 788-806.
- BALISTRIERI L. S. and MURRAY J. W. (1982) The adsorption of Cu, Pb, Zn, and Cd on goethite from major ion seawater. *Geochim. Cosmochim. Acta* **46**, 1253-1265.
- BALISTRIERI L. S., BREWER P. G. and MURRAY J. W. (1981). Scavenging residence times of trace metals and surface chemistry of sinking particles in the deep ocean. *Deep-Sea Res.* **28A**, 101-121.
- BILLON A. (1982) Fixation d'éléments transuraniens à différents degrés d'oxydation sur les argiles. In *Proc. Symp. on Migration in the Terrestrial Environment of Long-lived Radionuclides from the Nuclear Fuel Cycle*, Knoxville, TN, 27-31 July 1981. IAEA, Vienna.
- BONDIETTI E. A. and REYNOLDS S. A. (1976) Field and laboratory observations on plutonium oxidation states. In *Proceedings, Actinide-Sediment Reactions Working Meeting*, Seattle, 10-11 Feb. 1976. (ed. L. L. AMES). BNWL-2117.
- BONDIETTI E. A. and TRABALKA J. R. (1980) Evidence for plutonium (V) in an alkaline, freshwater pond. *Radiochem. Radioanal. Letters* **42**, 169-176.
- BONDIETTI E. A., REYNOLDS S. A. and SHANKS M. H. (1976) Interactions of plutonium with complexing substances in soils and natural waters. In *Transuranium nuclides in the environment*, Proc. Symp., San Francisco, 17-21 November 1975. IAEA, Vienna.
- BOWEN V. T., NOSHKIN V. E., LIVINGSTON H. D. and VOLCHOK H. L. (1980) Fallout radionuclides in the Pacific Ocean: vertical and horizontal distributions, largely from GEOSECS stations. *Earth Plan. Sci. Lett.* **49**, 411-434.
- CHOPPIN G. R. (1983) Aspects of plutonium solution chemistry. In *Plutonium Chemistry* (eds. W. T. CARNALL and G. R. CHOPPIN), pp. 213-230. ACS Symposium Series 216, ACS.
- CHOPPIN G. R. and MORSE J. W. (in press) Laboratory studies of plutonium in marine systems. In *Symposium on Environmental Research for Actinide Elements*.
- CLEVELAND J. M. (1979) Critical review of plutonium equilibria of environmental concern. In *Chemical Modeling in Aqueous Systems* (ed. E. A. JENNE). Amer. Chem. Soc., Washington, D.C.
- CONNICK R. E. (1949) The mechanism of disproportionation of plutonium (V). In *The Transuranium Elements* (eds. G. T. SEABORG, J. J. KATZ and W. MANNING). McGraw-Hill, New York.
- DAVIS J. A., JAMES R. O. and LECKIE J. O. (1978) Surface ionization and complexation at the oxide/water interface. I. Computation of electrical double layer properties in simple electrolytes. *J. Coll. Interf. Sci.* **63**, 480-499.
- DE REGGE P., BONNE A., HUYS D. and HEREMANS R. (1980) Experimental investigation of the behavior of long-lived radioisotopes in a natural water clay system. In *Marine Radioecology, Proc., 3rd NEA Seminar, Tokyo, 1-5 October 1979*. OECD.
- DUURSMA E. K. and PARSI P. (1974) Distribution coefficient of plutonium between sediment and seawater. In *Activities of the International Laboratory of Marine Radioactivity, 1974 Reports*. IAEA, Vienna.
- FOTI S. C. and FREILING E. C. (1964) The determination of the oxidation states of tracer uranium, neptunium and plutonium in aqueous media. *Talanta* **11**, 385-392.
- GROMOV V. V. and SPITSYN V. I. (1974) Sorption of  $^{239}\text{Pu}$ ,  $^{106}\text{Ru}$ , and  $^{99}\text{Tc}$  by bottom sediments of the Pacific Ocean. *Soviet Radiochem.* **16**, 157-162.
- KENNEY-KENNICUTT W. L. and MORSE J. W. (1985) The redox chemistry of  $\text{Pu(V)} \text{O}_2^+$  interaction with mineral surfaces in dilute solutions and seawater. *Geochim. Cosmochim. Acta* (in press).
- KIM J. I., LIERSE C. H. and BAUMGARTNER F. (1983) Complexation of the plutonium (IV) ion in carbonate-bicarbonate solutions. In *Plutonium Chemistry* (eds. W. T. CARNALL and G. R. CHOPPIN). ACS Symposium Series 216, ACS, 317-334.
- MAGNUSSON L. B. and LACHAPPELLE T. J. (1948) The first isolation of element 93 in pure compounds and a determination of the half-life of  $^{93}\text{Np}^{237}$ . *J. Am. Chem. Soc.* **70**, 3534.
- METIVIER H. and GUILLAUMONT R. (1976) Hydrolysis and complexing of tetravalent plutonium. *J. Inorg. Nucl. Chem., Supplement 1976* 179-183.
- MINER F. J. and SEED J. R. (1967) Radiation chemistry of plutonium nitrate solutions. *Chem. Rev.* **67**, 299-315.
- MOSKVIN A. I. and GEL'MAN A. D. (1958) Determination of the composition and instability constants of oxalate and carbonate complexes of plutonium (IV). *Russ. J. Inorg. Chem.* **3**(4), 198-216.
- NASH K., SHERMAN F., FIEDMAN A. M. and SULLIVAN J. C. (1981) Redox behavior, complexing, and adsorption of hexavalent actinides by humic acid and selected clays. *Env. Sci. Technol.* **15**, 834-837.
- NELSON D. M. and LOVETT M. B. (1978) Oxidation state of plutonium in the Irish Sea. *Nature* **236**, 599-601.
- NELSON D. M. and LOVETT M. B. (1981) Measurements of the oxidation state and concentration of plutonium in interstitial waters of the Irish Sea. In *Impacts of Radionuclide Releases into the Marine Environment, Proc., Symp., Otaniemi, 30 June-4 July 1975*. IAEA, Vienna.
- NELSON D. M. and ORLANDINI K. A. (1979) Identification of Pu (V) in natural waters. In *Radiological and Environmental Research Division Annual Report, ANL-79-65, Part III*, pp. 57-59.
- NELSON D. M., KARTTUNEN J. O., ORLANDINI K. A. and LARSEN R. P. (1980) Influence of dissolved organic carbon on the sorption of plutonium to natural sediments. In *Radiological and Environmental Research Division Annual Report, ANL-80-115, Part III*, pp. 19-25.
- NELSON D. M., KARTTUNEN J. O. and MEHLHOFF P. (1981) Influence of colloidal dissolved organic carbon (DOC) on the sorption of plutonium in natural sediments. In *Radiological and Environmental Research Division Annual Report, ANL-81-115, Part III*, pp. 48-52.
- PROUT W. E. (1957) Adsorption of radioactive wastes by Savannah River Plant soil. *Soil Science* **84**, 13-17.
- RABIDEAU S. W. (1957) The kinetics of disproportionation of plutonium (V). *J. Amer. Chem. Soc.* **79**, 6350-6353.
- RHODES D. W. (1957) Adsorption of plutonium by soil. *Soil Sci.* **84**, 465-471.
- ROZZELL T. C. and ANDELMAN J. B. (1971) Plutonium in the water environment. II. Sorption of aqueous plutonium on silica surfaces. In *Nonequilibrium Systems in Natural*

*Water Chem.*  
ACS.

SANCHEZ A. L. (in press) *behavior of*  
University of  
SANCHEZ A. L. (in press) *ronments*.  
SANCHEZ A. L. *tribution co*  
tulates in  
mental Mig  
TN, 27-31  
SCHINDLER F. *interfaces*.  
*Interfaces*.  
Arbor Sci.  
SCHWAB A. L. *namie dat*  
Abstracts  
tle, March  
SIBLEY T. H.  
and ALBEF

10

- and HEREMANS R. (1980) The behavior of long-lived actinides in a clay system. In *Marine Radioactivity*, Tokyo, 1-5 October.
- (1974) Distribution coefficient of plutonium in seawater. In *Activities of Marine Radioactivity*.
- (1974) The determination of plutonium, neptunium and plutonium-239. *Marine Chemistry* 11, 385-392.
- (1974) Sorption of  $^{239}\text{Pu}$  on goethite from the Pacific Ocean.
- FORSE J. W. (1985) The interaction with mineral surfaces. *Geochim. Cosmochim. Acta* 49, 101-110.
- HARTNER F. (1983) Complexation in carbonate-bicarbonate systems. *Chemistry* (eds. W. T. CARLSON) Symposium Series 216, American Chemical Society, Washington, D.C.
- LE T. J. (1948) The first actinide compounds and a determination of their properties. *J. Am. Chem. Soc.* 70, 1-10.
- LE T. J. (1976) Hydrolysis and complexation. *J. Inorg. Nucl. Chem.* 31, 1-10.
- (1976) Radiation chemistry of plutonium. *Rev. Mod. Phys.* 48, 299-315.
- (1958) Determination of the rate constants of oxalate and oxalate (IV). *Russ. J. Inorg. Chem.* 3, 1-10.
- M. and SULLIVAN J. C. (1978) Adsorption, desorption, and adsorption of plutonium on and selected clays. *Env. Sci. Technol.* 12, 1-10.
- (1978) Oxidation state of plutonium. *Science* 236, 599-601.
- (1981) Measurements of the distribution of plutonium in the environment. *Proc. Symp. on the Impacts of Radionuclides in the Environment*, IAEA, Vienna.
- A. (1979) Identification of plutonium. *Radiochemical and Environmental Report*, ANL-79-65, Part I.
- ORLANDINI K. A. and LARSEN R. P. (1978) Adsorption of dissolved organic carbon on natural sediments. In *Radiochemical and Environmental Research Division Annual Report*, ANL-78-65, Part III, pp. 64-68.
- and MEHLHOFF P. (1981) Adsorption of organic carbon (DOC) on natural sediments. In *Radiochemical and Environmental Research Division Annual Report*, ANL-79-65, Part I, pp. 13-17.
- (1974) Radioactive wastes by Saegert. *Science* 84, 13-17.
- (1974) Studies of disproportionation of plutonium by soil. *Soil Sci. Soc. Am.* 38, 6350-6353.
- B. (1971) Plutonium in the environment. *Systems in Natural*
- Water Chemistry* (ed. J. D. HEM). Adv. Chem. Ser. #106, ACS.
- SANCHEZ A. L. (1983) *Chemical speciation and adsorption behavior of plutonium in natural waters*. Ph.D. dissertation, University of Washington, Seattle, WA.
- SANCHEZ A. L., MURRAY J. W., SCHELL W. R. and MILLER L. (in press) Fallout plutonium in two oxic-anoxic environments. *Limnol. Oceanogr.*
- SANCHEZ A. L., SCHELL W. R. and SIBLEY T. H. (1982) Distribution coefficients for plutonium and americium on particulates in aquatic environments. In *Proc. Symp. Environmental Migration of Long-Lived Radionuclides*, Knoxville, TN, 27-31 July 1981. IAEA, Vienna.
- SCHINDLER P. W. (1981) Surface complexes at oxide-water interfaces. Ch. 1. In *Adsorption of Inorganics at Solid-Liquid Interfaces* (eds. M. A. ANDERSON and A. J. RUBIN). Ann Arbor Sci. Publ., Ann Arbor, Michigan.
- SCHWAB A. P. and FELMY A. R. (1983) *Critical thermodynamic data evaluation and recalculation for Pu and Np*. Abstracts 185th Amer. Chem. Soc. National Meeting, Seattle, March 1983. p. 63.
- SIBLEY T. H., CLAYTON J. R., WURTZ E. A., SANCHEZ A. L. and ALBERTS J. J. (1984) Effects of dissolved organic compounds on the adsorption of transuranic elements. In *Complexation of Trace Metals in Natural Waters* (eds. C. J. M. KRAMER and J. C. DUINKER). Martinus Nijhoff/Dr. W. Junk Publishers, The Hague, Netherlands.
- SIMPSON H. J., TRIER R. M., OLSEN C. R., HAMMOND D. E., EGE A., MILLER L. and MELACK J. M. (1980) Fallout Plutonium in an alkaline, saline lake. *Science* 207, 1071-1073.
- WAHLGREN M. A., NELSON D. M., ORLANDINI K. A. and LARSEN R. P. (1978) Plutonium in fresh water. In *Radiochemical and Environmental Research Division Annual Report*, ANL-78-65, Part III, pp. 64-68.
- WESTALL J. C. and HOHL H. (1980) A comparison of electrostatic models for the oxide/solution interface. *Adv. Coll. Inter. Sci.* 12, 265-294.
- WESTALL J. C., ZACHARY J. L. and MOREL F. M. M. (1976) MINEQL, a computer program for the calculation of chemical equilibrium composition of aqueous systems. Water Qual. Lab., Tech. Note No. 18, Dept. of Civil Eng., Mass. Inst. of Tech., Cambridge.
- YATES D. E., LEVINE S. and HEALY T. W. (1974) Site binding model of the electrical double layer at the oxide/water interface. *J. Chem. Soc. Faraday Trans. (1)* 70, 1807-1818.

11/11